

# EXHIBIT D

# POLYMER STABILIZERS. A SURVEY WITH REFERENCE TO POSSIBLE APPLICATIONS IN THE CONSERVATION FIELD

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**Abstract**—A survey of the most common classes of polymer stabilizers is presented. Topics which are discussed include: chemical composition, inhibition mechanisms, areas of application, synergism, compatibility of additives and substrates, and evaluation of the performance of stabilizers. Hindered amine light stabilizers and benzotriazole and benzophenone type ultraviolet absorbers are particularly recommended for conservation materials. In order to prevent physical loss of additives by volatilization or exudation, high molecular weight stabilizers which are chemically compatible with the substrate should be used. Before using additives in conservation materials they should be scrutinized for negative side effects in properly designed accelerated aging tests.

## 1 Introduction

A variety of antioxidants and other stabilizing additives for polymeric materials is currently available. The additives, at low concentrations (typically 0.25–3%), inhibit degradation processes that cause loss of the original properties of the materials. Many new stabilizers developed during the last decade have found wide application in the plastics and coatings industry. A few papers discussing the effect of some stabilizing additives on picture varnishes and inpainting media have appeared recently [1–4]. Feller has described the inhibiting effect of a few stabilizers on the cross-linking process of polymers and copolymers of n-butyl- and isobutyl-methacrylate [5, 6]. Incorporation of stabilizers into conservation materials may indeed offer a viable means of prolonging their useful life. The most obvious area of application is in (clear) coatings, which deteriorate more rapidly than most materials due to a large surface to volume ratio. But other conservation materials, such as adhesives and consolidants, could profit from the incorporation of stabilizers as well.

It is likely that stabilizers will find application in the conservation field more often in the future.

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*Studies in Conservation* 33 (1988) 9–22

Stabilizers, however, may have negative effects, notably staining by either the parent product or decomposition products of the additive [7], and migration of the additives to the surface. Knowledge of the properties of stabilizing additives and proper testing of their performance are essential. A general discussion of the chemistry of stabilizing additives therefore seems in order.

The purpose of this paper is to give a survey of the most common classes of stabilizing additives. Chemical composition, inhibition mechanisms and areas of application will be discussed. The difference between stabilizers designed to protect polymers at high temperatures (heat stabilizers) and those designed to protect polymers against degradation by ultraviolet light (light stabilizers) will be stressed. Other subjects which will be discussed briefly are: synergism between additives, compatibility of additives and substrates, incompatibility between additives, staining due to decomposition products of additives and evaluation of the performance of the additives. It should be pointed out that the chemistry of stabilizing additives is quite complex and in the framework of this publication can be discussed only in the most general terms. For detailed information on the subject the reader is referred to the original literature\*.

Examples of commercially available stabilizers are included in this paper, with some structural formulae appearing in an Appendix, and a list of suppliers. This list, however, is not exhaustive, and is restricted to suppliers in the USA.

## 2 Autoxidation and general mechanisms of inhibition

Organic materials deteriorate due to autoxi-

\*Many review articles have appeared in the series *Developments in Polymer Stabilisation* (ed. G. SCOTT, Elsevier Applied Science Publ., London).

E. René de la Rie

dation, i.e. reactions with oxygen in the air [8]. These reactions cannot be discussed in detail within the context of this paper. Nevertheless, in order to be able to discuss the inhibition of the process by stabilizing additives, a brief summary of the autoxidation process is necessary.

The primary reactions participating in the autoxidation process of organic materials are listed in Figure 1. Autoxidation involves a radical chain mechanism during which initially *hydroperoxides* (ROOH) are formed. The pro-

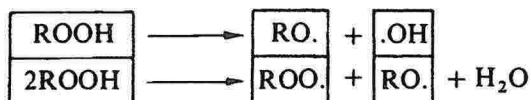
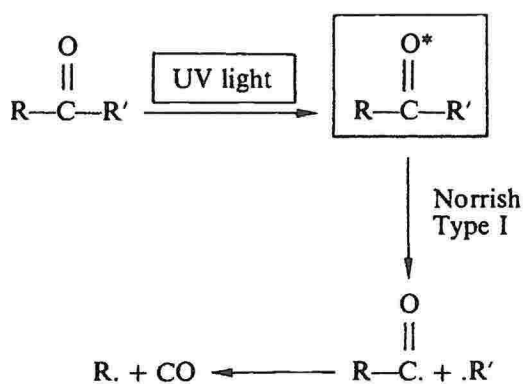
cess starts with homolytic bond cleavage, i.e. the breaking of a covalent bond between two atoms in a molecule, leaving two free radicals. Carbonyl groups (R-CO-R'), for example, undergo scission reactions (called Norrish type I and II reactions) under the influence of ultraviolet light and are therefore an important source of free radicals in materials which contain such groups in their molecular structure [9]. Hydroperoxides are the chief source of free radicals in many materials, since they decompose readily to yield peroxy (ROO.), alkoxy (RO.) and hydroxy (HO.) radicals. Owing to the fact that hydroperoxides are the initial products of autoxidation, the process is autocatalytic.

In the *initiation step* of the chain mechanism an initiator of radical chain reactions (I.) (which can be any radical) abstracts a hydrogen atom from an organic molecule (RH) to produce an alkyl radical (R.). During the *propagation steps* highly reactive alkyl radicals react rapidly with oxygen to form peroxy radicals (ROO.), which are able to abstract other hydrogen atoms to form hydroperoxides (ROOH) and new alkyl radicals. The latter reaction (hydrogen abstraction by peroxy radicals) is the rate determining step of the propagation reactions, since the reaction of alkyl radicals with oxygen is extremely fast. Peroxy radicals are therefore the most abundant free radicals. If uninhibited, the radical chain ends when two free radicals react with each other (*termination steps*). Under normal circumstances termination reactions between peroxy radicals will be the most important ones (see Figure 1).

Certain functional groups undergo autoxidation reactions more easily than others. Carbonyl groups and other functional groups which absorb near ultraviolet light may be responsible for the production of radicals through scission reactions. Hydrogen atoms in  $\alpha$ -positions to functional groups, such as carbon-carbon double bonds and carbonyl groups, or hydrogen atoms attached to tertiary carbon atoms, are more easily abstracted than others. The presence of such groups, therefore, causes a material to be vulnerable to autoxidation.

Stabilizing additives may interfere with the above reactions in a number of different ways. Antioxidants inhibit the autoxidation process by reactions with free radicals (*radical scavenging*) or by reaction with hydroperoxides (*preventive*

*Homolytic bond cleavage:*



*Initiation*



*Propagation*



*Termination*



Figure 1 Autoxidation reactions. R. = alkyl radical, I. = initiator of radical reactions (any radical, e.g. ROO. or RO.). See text for further explanations. Species which may be removed from the process by stabilizing additives are placed in boxes. \*denotes an excited state.



### Polymer stabilizers

*mechanism*) [8, 10]. Radical scavengers remove chain propagating radicals such as peroxy and alkoxy radicals, thus interrupting the chain mechanism. They are therefore also referred to as *chain-breaking antioxidants*. Preventive antioxidants decompose hydroperoxides in a non-radical process to prevent the production of free radicals from them. Ultraviolet absorbers protect materials by absorbing ultraviolet light and dissipating the energy in the form of thermal energy. In addition some stabilizers may counteract the harmful influence of UV radiation by quenching of excited states. A discussion of some of the most important classes of stabilizers follows.

### 3 Classes of stabilizers

#### 3.1 Hindered phenols

Probably the best known class of antioxidants is that of the hindered phenols. They have in com-

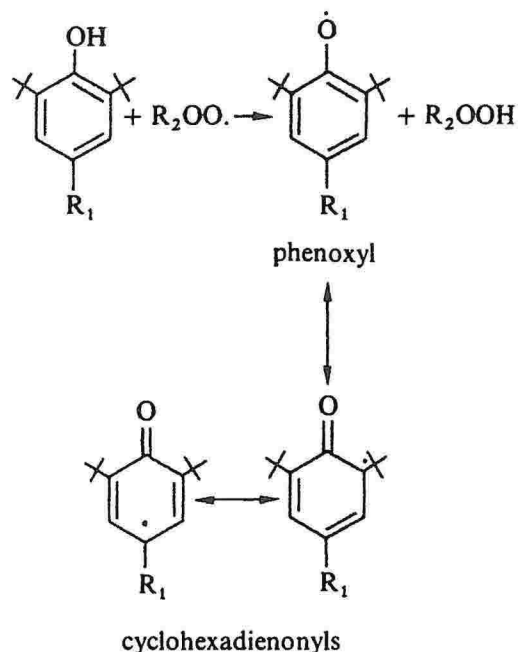


Figure 3

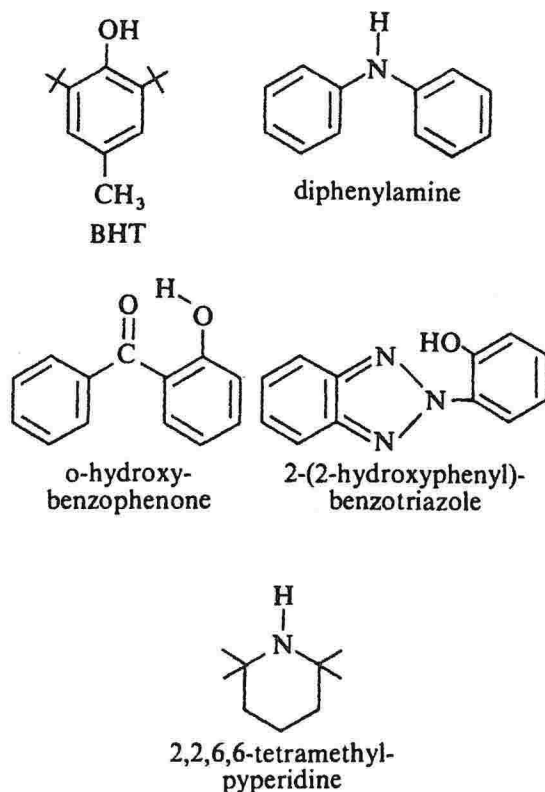


Figure 2 Some structural elements of polymer stabilizers.

mon a phenolic group with at least one bulky group such as a tertiary butyl group in the ortho position. Butylated hydroxytoluene (BHT) is one of the simplest examples of a hindered phenol (see Figure 2). Most current phenolic stabilizers of polymers are molecules larger than BHT, thus reducing the risk of loss of the additive by volatilization during high temperature processing. Furthermore, polymer stabilizers commonly have more than one functional group with antioxidant activity in their molecular structure.

Hindered phenols are radical scavengers since they react with peroxy (ROO·) and alkoxy radicals (RO·) to form phenoxy radicals, which are relatively stable because of resonance stabilization and steric hindrance [11, 12] (see Figure 3). Hindered phenols break the radical chain mechanism since phenoxy radicals do not abstract hydrogen atoms from organic molecules. Phenoxy radicals can also be represented by resonance structures in which the unpaired electron resides on a carbon atom (cyclohexadienonyls—see Figure 3). Reaction with another peroxy radical is therefore possible (see Figure 4). Consequently, monohydric phenolic antioxidants ideally terminate two kinetic oxidation chains. Cyclo-



E. René de la Rie

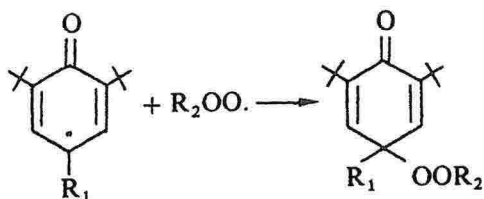


Figure 4

hexadienonyls, however, become bonded to the resin molecules in the process through peroxidic bonds. These as well as the carbonyl group make the structure vulnerable to reactions induced by light and heat. The resulting fragments act as initiators of radical chain reactions. The overall stoichiometric coefficient for phenolic antioxidants, therefore, is smaller than two. It is important to note that the antioxidant activity of hindered phenols is essentially not catalytic and that consequently the additives are used up in the stabilization process.

As phenolic antioxidants are heat stabilizers, they give protection against thermally induced autoxidation at room temperature as well as elevated temperatures. However, they generally perform poorly when light is present, due to the poor light stability of the additives themselves [11]. This makes the additives of limited use for most applications where photochemical degradation reactions play a role. At best they may improve the performance of light stabilizers when used in conjunction with them.

Hindered phenols undergo a series of complex transformations during autoxidation [11, 12]. Some transformation products of phenolic antioxidants have antioxidant activity: unfortunately, many of these products are colored. An example of the formation of a colored product (quinone methide) from BHT is given in Figure 5. Many more colored products with

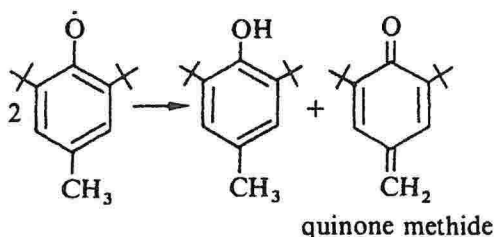


Figure 5

12

complex structures are formed from phenolic antioxidants.

Commercial examples of phenolic antioxidants are Ultrinox 226, 246, 257 and 276 (Borg-Warner), Irganox 259, 1076, 1010, 3114 and 3125 (Ciba-Geigy), Cyanox 425 and 2246 (Cyanamid), Ethanox 330, 376 and 702 (Ethyl), Oxi-Chek 114, 116 and 414 (Ferro), Good-rite 3112 (Goodrich), Hostanox 03 (Hoechst), Topanol CA (ICI), Wytox PAP (Olin), Naugard BHT, SP, 76 and 431, and Naugawhite (Uniroyal) and Vanox SWP, ZS, 100, 102, 1290, 1320 and 2246 (Vanderbilt). Polyfunctional stabilizers containing phenolic groups are Ultrinox 236 and 254 (Borg-Warner), Irganox 565, 1035, 1098 and 1425, Irgastab 2002 and Tinuvin 144 (Ciba-Geigy), Cyanox 1735 and 1790 (Cyanamid), Ethanox 736 (Ethyl) and Naugard XL-1 and 492 (Uniroyal).

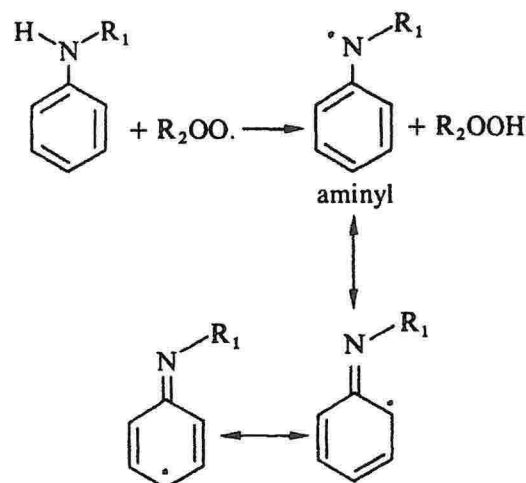


Figure 6

### 3.2 Aromatic amines

Aromatic amines are chain-breaking antioxidants that undergo reactions similar to those of hindered phenols [8, 10, 11, 13]. They are powerful heat stabilizers; however, they have the serious disadvantage of forming colored transformation products [12, 14]. It is for this reason that they are used mainly as stabilizers in carbon black containing rubbers. Their stabilizing mechanism is similar to that of hindered phenols (see Figure 6). The aminyl radicals formed dur-

*Studies in Conservation* 33 (1988) 9-22

### Polymer stabilizers

ing reactions with peroxy and alkoxy radicals are again relatively stable through resonance stabilization. Many of the commercial amines are derivatives of diphenylamine (see Figure 2).

Aminyls undergo very complex transformations which lead to products with pro-oxidant as well as antioxidant activity. Coupling reactions between aminyl radicals lead to dark colored polyconjugated systems. Aromatic amines, like hindered phenols, are essentially used up during the stabilizing process, and they have very low photochemical stability. Because of their discoloring properties they are not likely to be of much interest to the conservation field.

Commercial examples of aromatic amines are Irganox LO 6 and L57 (Ciba-Geigy), Good-rite 3120X1, 3140, 3152X1, 3190X29, 3191 and 3185X1 (Goodrich), DPA, Naugard J and 445, Naugalube 438, 438L, 438R and PANA (Uniroyal) and Agerite DPPD, Stalite and White, Vanox AM, ODP, 3C, 6H, 12 and 200 (Vanderbilt). Commercial examples of polyfunctional stabilizers containing aromatic amine groups are Irganox 565 (Ciba-Geigy) and Good-rite 3920X3 (Goodrich).

### 3.3 Sulfur compounds

Various sulfur compounds have antioxidant activity. The most important are organic sulfides, which act as hydroperoxide decomposers rather than as radical scavengers [8, 10, 12, 15, 16]. They are mostly used in conjunction with phenolic antioxidants since they exert little antioxidant, or even a pro-oxidant, effect by themselves but synergistically enhance the stabilizing effect of hindered phenols [17]. Sulfides reduce hydroperoxides to their corresponding alcohols in a non-radical process. The sulfide is thereby oxidized to a sulfoxide:



Transformation products of sulfoxides, however, have antioxidant activity as well. Sulfoxides break down rapidly to give sulfenic acids and a variety of other transformation products [15-17]. Many of these transformation products catalytically decompose hydroperoxides but some inhibition by radical scavenging may occur as well. At elevated temperatures in particular a variety of transformation products is formed with antioxidant activity [12, 15-17]. Mixtures of hindered phenols and sulfides, and phenolic sulfides (additives that combine phenolic and

sulfide groups in their molecular structure), therefore, are used predominantly for stabilization of rubbers and plastics during processing stages which require high temperatures. Care should be taken with the use of sulfides in materials that contain metal ions (or that are in contact with metal ions) which react with sulfides to form dark colored products (e.g. lead ions).

Commercial examples of sulfides are Cyanox LTDP, MTDP, STDP, 711 and 1212 (Cyanamid) and Hostanox SE2 and SE10 (Hoechst). Commercial examples of phenolic sulfides are Ultrinox 236 (Borg-Warner), Irganox 1035 (Ciba-Geigy) and Ethanox 736 (Ethyl). Irganox 565 (Ciba-Geigy) is a polyfunctional stabilizer containing sulfide groups.

### 3.4 Phosphorus compounds

Organic phosphites and phosphonites are efficient hydroperoxide decomposers [18-20]. Phosphites reduce hydroperoxides to their corresponding alcohols in a non-radical process during which the phosphites are oxidized to phosphates:



R in the above equation is either an alkyl or an aryl group. Again, other reactions, notably between phosphites and chain propagating radicals, are possible as well. Like the sulfides, phosphites are mostly used in combination with hindered phenols for the stabilization of polymers at elevated temperatures. Synergism has been demonstrated to occur between phosphites and phenols as well as between phosphites and certain transition metal complexes. A remarkable property of phosphites is that they appear to suppress the discoloring nature of stabilizers such as amines and phenols [19]. A serious drawback of phosphites is their tendency to undergo hydrolysis. Small amounts of a base are often added to commercial phosphites to prevent decomposition due to hydrolysis; aromatic phosphites are more resistant to hydrolysis than aliphatic phosphites. Some newly developed phosphites and phosphonites have much improved resistance to hydrolysis [21].

Commercial examples of phosphites and phosphonites are Irgafos 168 and P-EPQ (Ciba-Geigy), Wytox 312 (Olin) and Naugard P, PHR, 512 and 524 (Uniroyal). Borg-Warner carries a multitude of phosphites under the tradename



Weston. Commercial examples of phenolic phosphites are Cyanox 1735 (Cyanamid) and Naugard 492 (Uniroyal). Ciba-Geigy sells blends of Irgafos 168 and various phenolic antioxidants under the name Irganox B-Blends.

### 3.5 Metal chelates

Metal chelates (metal complexes) and ions may have a catalytic as well as inhibiting effect on autoxidation [8, 22]. The catalytic effect of trace quantities of metal ions, such as lead, manganese and cobalt ions, on autoxidation processes has been known for a long time. Metal ions, in the form of metal soaps (siccatives), have been added for centuries to drying oils to promote the autoxidative drying process of oil paint. They catalyze autoxidation by a redox mechanism, during which hydroperoxides are decomposed into radical fragments (see Figure 7) [22]. Metal

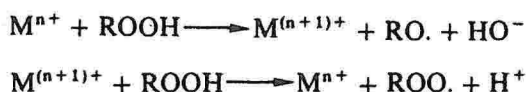
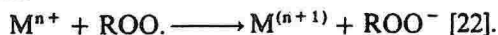


Figure 7 Catalytic decomposition of hydroperoxides by a metal ion with two oxidation states.

ions with two stable oxidation states such as  $\text{Co}^{2+/3+}$  are the most effective. The harmful effect of trace quantities of metal ions can be counteracted with so-called metal deactivators. These compounds are capable of forming complexes with the metal ions. If the concentration of metal ions increases beyond a certain value, however, the catalytic effect of the ions is suddenly converted into an inhibiting one. Inhibition may occur through reaction with chain propagating radicals such as peroxy radicals:



Nickel complexes, which are efficient light stabilizers, may work both by a radical scavenging mechanism and by a quenching mechanism (i.e. the energy absorbed by chromophores in the substrate is transferred to the stabilizer molecule before it leads to decomposition) [23]. It has also been claimed, however, that radical scavenging and hydroperoxide decomposition are the most important inhibition mechanisms [24]. Although the mechanisms of metal chelates are still a matter of debate, it is believed that complex for-

mation between hydroperoxides and metal ions is the key to catalyst-inhibitor conversion [22]. If the metal ion is present at a concentration higher than that of hydroperoxides, free metal ions are available for the reactions with chain propagating radicals, whereas at lower concentrations breakdown of hydroperoxides into radical fragments is the dominating reaction.

Polyfunctional stabilizers have been developed which combine metal complexes with other functional groups. Metal complexes containing sulfur ligands are very efficient heat stabilizers [22, 25]. Nickel complexes (also called nickel quenchers) usually have a green color which makes the additives of limited use for clear coatings. Dark colored products may be formed as well.

Commercial examples of polyfunctional nickel complexes are Irgastab 2002 (Ciba-Geigy), Cyasorb UV 1084 (Cyanamid), UV-Chek AM 104, 105 and 205 (Ferro), Hostavin VP NiCS 1 (Hoechst) and Conservator 77N and 125 N (Tennessee Valley).

### 3.6 Ultraviolet absorbers

Compounds absorbing ultraviolet light have a stabilizing function in materials exposed to this form of radiation. Incorporation of UV-absorbers reduces photochemical homolysis responsible for radical production: carbon black present in rubber has this effect. In many applications, however, only colorless compounds are acceptable. Several ultraviolet absorbers are available which absorb strongly in the 300–400nm region, but do not do so at longer wavelengths in the visible range of the electromagnetic spectrum. The most important ultraviolet absorbers are derivatives of ortho-hydroxybenzophenone or of 2-(2-hydroxyphenyl)-benzotriazole (see Figure 2). Both compounds absorb in the 300–400nm region and are able to dissipate the absorbed energy rapidly as harmless thermal energy. A tautomeric mechanism is believed to be responsible for the rapid radiationless return to the ground state of the molecules (see Figure 8) [23].

Although radical scavenging properties have been claimed to exist for benzotriazoles [23, 26], it is likely that benzophenones are much more prone to such reactions than benzotriazoles [24, 27]. Consequently, benzotriazoles last much longer than benzophenones in polyolefins [28].



### Polymer stabilizers

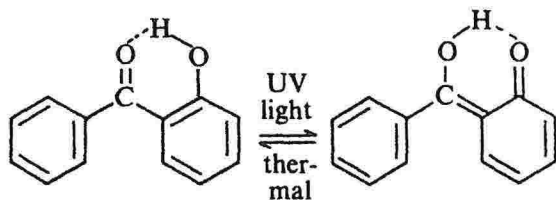


Figure 8

Benzotriazoles also have higher extinction coefficients than benzophenones [29]. Quenching of excited states has been shown to occur with benzophenones [30] as well as benzotriazoles [24, 31]. Furthermore, benzotriazoles [23, 32] and benzophenones [30] enhance the effect of hindered amine light stabilizers (HALS—see section 3.7) synergistically.

It has been reported that benzotriazoles break down rapidly in polyolefins once oxidation products such as ketones start to build up, due to reactions with these products [24, 30]. This would have implications for their use in materials which have a high carbonyl content when fresh, such as picture varnishes based upon dammar and ketone resin. The present author has found that benzotriazoles break down relatively fast in films of dammar and ketone resin during accelerated aging in a fadeometer [33]. However, this may also be caused by reactions with radicals, which are produced at very high concentrations in these unstable products.

Since the primary action of ultraviolet absorbers is absorption of ultraviolet light, they generally do not have a large effect in thin films. Only in deeper layers can complete screening from ultraviolet light be achieved. A reduction in intensity to 1% at a depth of 0.1mm can be achieved with benzotriazoles at concentrations of 0.25–0.50%. Therefore in varnish films of, say, 10–20µm thickness not much should be expected from these compounds, especially if one realizes that photooxidation generally occurs only to a depth of about 10µm [34, 35]. However, synergism may occur between HALS and ultraviolet absorbers even when they are used in thin films [33].

Ultraviolet absorbers are most effective when they are used as protectors of layers behind the surface layer containing the additive. When a two-coat varnish system is used, such as an acrylic varnish over ketone resin [36], incorpo-

ration of a UV-absorber into the acrylic varnish may give protection to the ketone resin layer underneath.

Commercial examples of benzophenones are Uvinul 400, 408, 490, M-40, D-49 and D-50 (BASF), Cyasorb UV 9, 24, 531 and 2126 (Cyanamid), UV-Chek 300 and 301 (Ferro) and Hostavin AR08 (Hoechst); commercial examples of benzotriazoles are Tinuvin P, 326, 327, 328, 900 and 1130 (Ciba-Geigy) and Cyasorb UV 5411 (Cyanamid). Ciba-Geigy is a major supplier of benzophenones outside the USA.

### 3.7 Hindered amine light stabilizers

Hindered amine light stabilizers (HALS) are a relatively new class of stabilizers. They have been proved to be very powerful light stabilizers particularly in polyolefins, such as polyethylene and polypropylene, which are polymers that degrade rapidly without stabilization. Their mechanism of stabilization is both complex and unusual. Despite the fact that much literature on these additives has appeared in the past decade, some of the mechanisms have not yet been fully explained. HALS are primarily radical scavengers; however, transformation products of the additives rather than the original material are the true antioxidants. HALS work at least in part catalytically, for these transformation products can be regenerated [23, 37–41]. This fact makes HALS very powerful compared to stoichiometric antioxidants such as hindered phenols.

HALS have a secondary or tertiary amine group in common, usually in a ring structure, with two methyl groups in each of the positions  $\alpha$  to the amine group. Most HALS are derivatives of 2,2,6,6-tetramethylpiperidine (see Figure 2). They react rapidly with peroxy radicals to give hindered nitroxyl radicals (see Figure 9).



Figure 9 Reactions of hindered amine light stabilizers.

Hindered nitroxyl radicals react efficiently with alkyl radicals, to give hydroxylamine ethers. The nitroxyl radical thus gets grafted onto the resin. A considerable amount of hydroxylamine ethers



may be formed, and in fact very little of the original HALS survives in polypropylene after brief exposure to ultraviolet light [40]. The hydroxylamine ethers are radical scavengers, which regenerate nitroxyl radicals through reaction with peroxy radicals (see Figure 9). The given reactions, however, are only a small part of the complex chemistry of hindered nitroxyl radicals [38, 39]. Discussion of all the reactions involved would be beyond the scope of this article. The most important property of HALS is that their stabilizing intermediates, nitroxyl radicals, can be regenerated, which makes the additives the most powerful light stabilizers currently available. In many tests HALS have outperformed any other class of stabilizers, and of all the additives discussed in this paper they are probably the most promising ones for the conservation field. Experiments at the Metropolitan Museum of Art have indicated that HALS may be effective in ketone resin, but that dammar, due to its very unstable nature, is probably very difficult to stabilize even with HALS.

HALS should also protect many substances against thermal degradation at ambient temperatures, and at moderately elevated temperatures if HALS of sufficiently high molecular weight are used [42, 43]. Acidic components may interfere with HALS, which have basic properties, and sulfur containing additives can also have antagonistic effects when used in conjunction with HALS [42].

Commercial examples of HALS are Tinuvin 292, 770 and 622 and Chimasorb 94 (Ciba-Geigy), Cyasorb UV 3346 (Cyanamid), Mixxim HALS 57, 62, 63, 67 and 68 (Fairmount) and Hostavin N20 (Hoechst). An example of a polyfunctional additive containing hindered amine groups is Tinuvin 144 (Ciba-Geigy).

#### 4 Synergism

Mixtures of two or more different types of additive often have a greater effect than the sum of the individual effects. The phenomenon is called synergism and it is the reason that additives are often used together and that additives have been developed which combine different functional groups in one molecule. *Homosynergism* between additives that stabilize by similar mechanisms (radical scavenging) has been observed between hindered phenols and aromatic amines.

*Heterosynergism* between aromatic amines and sulfides and between hindered phenols and sulfides has been observed as well [13]. Synergism has also been reported to take place between HALS and benzotriazole-type ultraviolet absorbers [23, 32] and between HALS and benzophenone-type ultraviolet absorbers [30].

Many polyfunctional additives are available, such as Tinuvin 144 (HALS and hindered phenol; Ciba-Geigy) and Cyanox 1735 (phenolic phosphite; Cyanamid).

#### 5 Volatility and chemical compatibility

When choosing a stabilizing additive, factors besides stabilizing functions should be taken into consideration. Additives may be lost through volatilization when exposed to elevated temperatures. However, volatilization and/or migration of additives at room temperature should be of concern to conservators, since this may take place during the long periods of time conservation materials are generally in use, even with stabilizers of relatively low volatility. Antioxidants with high molecular weight should therefore be used. Many additives with relatively high molecular weight and polymeric additives are currently available.

Another important factor is solubility and chemical compatibility with the substrate. Usually additives are mixed with the resin in solution, which makes solubility in a solvent in which the substrate is also soluble a requirement. Furthermore, additives have to be chemically compatible with the substrate, since otherwise they may migrate and exude.

Thus Tinuvin 328 is soluble in several solvents and compatible with many substrates, whereas Tinuvin 900 has less solubility and compatibility but higher molecular weight. The manufacturers' literature should be consulted in order to be able to make decisions along these lines.

#### 6 Evaluation of performance

For the evaluation of stabilizing additives it is inevitable that some sort of accelerated aging technique be employed. It is not possible to discuss the complexity of accelerated aging in this paper. However, it would be impossible to overemphasize the importance of choosing the proper accelerated aging technique and the right



### *Polymer stabilizers*

properties of the material under study for evaluation. Thus, aging under an appropriate light source is essential when the material to be tested is normally exposed to light. Xenon arcs, as employed in fadeometers and weatherometers, are recommended since their spectral output approaches that of daylight more closely than any other artificial lightsource [44]. At the Metropolitan Museum of Art a fadeometer which employs a borosilicate inner and a soda-lime outer filter around the xenon burner is used. This combination of filters eliminates the shorter wavelength UV radiation and allows for an approximation of daylight through window glass [35].

Care should be taken with the interpretation of the results of accelerated aging. Although some materials may not yellow as much during accelerated aging under intense light as during normal life, it is this author's opinion that aging under light is the only valid test for the study of the degradation and stabilization of materials normally exposed to light [7, 35]. The assumption that reaction mechanisms remain the same as long as radiation of the same spectral output is employed and that the reaction rate increases linearly with the intensity (i.e. that the so-called reciprocity law holds [45]) is not always justified. At the high light levels employed in accelerated aging devices, concentration levels of free radicals may be obtained that never occur during natural aging. This may result in different degradation mechanisms. It has been said, for example, that the hindered amines may perform better during natural aging than is predicted by accelerated aging studies [42].

Materials which are not exposed to light during their normal life could be tested in heat aging experiments. But if temperatures are used which are considerably higher than the ones the material is exposed to under normal circumstances, the danger exists of introducing new degradation reactions. Arrhenius plots [8] of a suitable parameter should be made to give some assurance that this is not the case. Heat aging tests of materials normally exposed to UV light are not likely to be valuable since photochemical oxidation is generally much more severe than thermal oxidation (below 200 °C [45]).

The solubility of materials is in general a good property to follow during accelerated aging, since oxidation or cross-linking may change that

property considerably. The more properties that are followed during the aging the better. Assessment of change using instrumental techniques, such as infrared and ultraviolet spectrophotometry, gel permeation chromatography, gloss measurements, etc., is preferred over visual assessment.

Individual systems may vary to a great extent in their response to stabilizing additives. Such systems should be tested individually: no assumptions should be made as to the effectiveness of a particular additive (combination) in one system based upon its effectiveness in other systems.

### **7 Conclusions**

Many stabilizing additives are currently available which could prolong the useful lives of conservation materials. Of all the additives discussed, hindered amine light stabilizers (HALS) and benzophenone and benzotriazole type ultraviolet absorbers are the most promising for the conservation field. Where light does not play a role, hindered phenols, in conjunction with phosphites and phosphonites, could be employed as stabilizers. It should be kept in mind, however, that HALS give protection against thermal degradation at room temperature as well as against photochemical degradation. Unless staining of the substrate is acceptable, aromatic amines should be avoided. To prevent physical loss of additives by volatilization or exudation, high molecular weight stabilizers which are chemically compatible with the substrate should be used.

Before stabilizers are used in conservation materials they should be scrutinized for negative side effects. Great care should be taken to insure that tests to evaluate their performance are designed to take into account all factors responsible for degradation of the substrate (as well as the additives) during normal life.

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E. René de la Rie

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#### Suppliers of polymer stabilizers\*

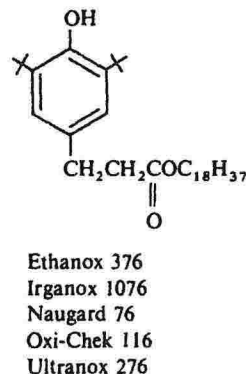
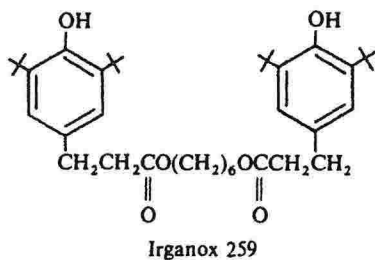
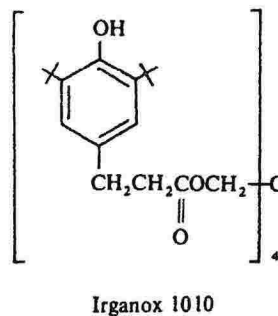
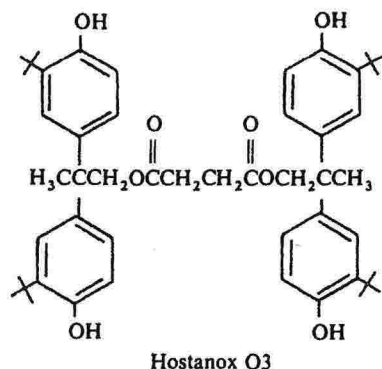
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 American Hoechst Corp., Route 202-206 North, Somerville, NJ 08876.  
 Borg-Warner Chemicals, International Center, Parkersburg, WV 26101.  
 Ciba-Geigy Corp., Additives Dept, 444 Saw Mill River Road, Ardsley, NY 10502.  
 Ethyl Corp., Chemicals Group, Ethyl Tower, 451

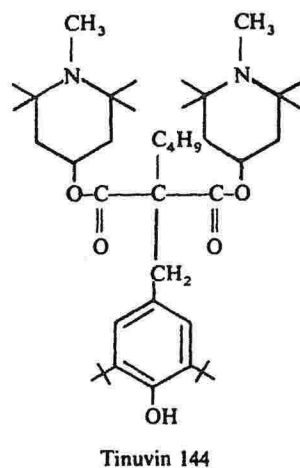
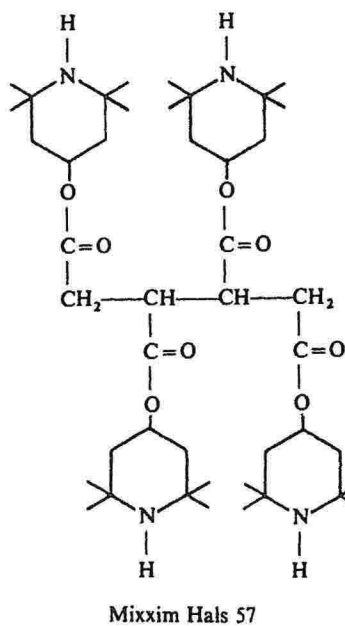
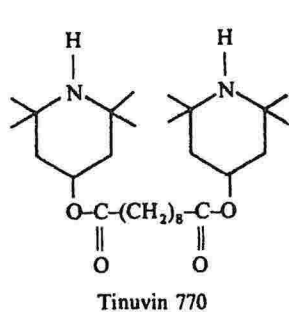
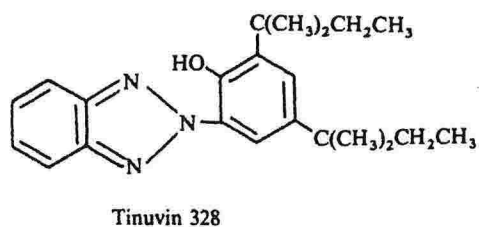
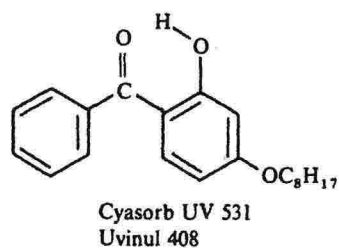
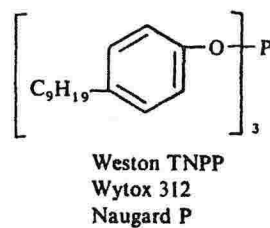
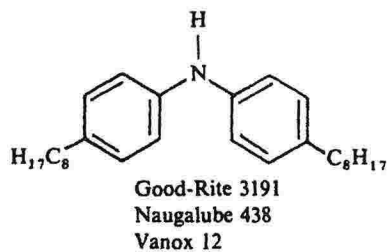
Florida, Baton Rouge, LA 70801.  
 Fairmount Chemical Co. Inc., Phoenix Polymer Additives Div., 117 Blanchard St, Newark, NJ 07105.  
 Ferro Corp., Bedford Chemical Div., 7050 Krick Road, Bedford, OH 44146.  
 ICI Americas, Chemicals Div., Wilmington, DE 19897.  
 Olin Corp., Chemicals Group, 120 Long Ridge Rd, Stamford, CT 06904.  
 Uniroyal Chemical Co., Middlebury, CT 06749.  
 Tennessee Valley Performance Products Inc., 1909 Manufacturers Road, Dayton, TN 37321.  
 R.T. Vanderbilt Co., Inc., 30 Winfield St, Norwalk, CT 06855.

\*This list is limited to suppliers in the USA. Additional suppliers can be found in the *Modern Plastics Encyclopedia*, McGraw-Hill Inc., New York.

#### Appendix: Molecular structures of some polymer stabilizers

The structures in this appendix are given solely for the purpose of illustration: inclusion in this list of a particular additive does not entail a recommendation.



*Polymer stabilizers*

E. René de la Rie

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ings Conservation Department of the Metropolitan Museum of Art in New York. *Author's address: Metropolitan Museum of Art, Fifth Avenue at 82nd Street, New York, NY 10028, USA.*

**Résumé**—Cet article passe en revue les stabilisateurs de polymères les plus employés, des points de vue suivants: composition chimique, mécanismes d'inhibition, surfaces d'application, synergie, compatibilité des additifs et des substrats, et évaluation de l'efficacité des stabilisateurs. On recommande particulièrement en conservation: pour les stabilisateurs de l'effet photochimique, les dérivés amino substitués, et pour les absorbants du rayonnement UV, les types benzotriazol et benzophénone. Dans le but de prévenir la perte d'additifs par volatilisation ou exsudation, on emploiera des agents stabilisateurs de masse moléculaire élevée qui soient chimiquement compatibles avec le substrat. Mais avant d'utiliser des additifs dans les produits de conservation, on doit en étudier les différents effets secondaires—qui peuvent

être négatifs—par des tests de vieillissement accéléré convenablement conduits.

**Zusammenfassung**—Der Beitrag gibt einen Überblick über die gebräuchlichsten Klassen von Polymerstabilisatoren, wobei er folgende Aspekte anschnaubt: chemische Zusammensetzung, Schutzmechanismen, Anwendungsgebiete, Synergismen, Verträglichkeit mit Zusätzen und Substraten und eine Bewertung der Wirksamkeit der Stabilisatoren. Sterisch gehinderte Amine als Lichtstabilisatoren und UV-Absorber vom Benzotriazol- und Benzophenon-Typ werden insbesondere für Konservierungsmaterialien empfohlen. Um einen Verlust derartiger Zusätze durch Verdampfung oder Auschwitzen zu verhindern, sollten hochmolekulare Stabilisatoren verwendet werden, die mit dem Substrat chemisch verträglich sind. Bevor allerdings derartige Zusätze in Konservierungsmaterialien verwendet werden, müssen diese in geeignet konzipierten Alterungstests sorgfältig auf negative Begleiterscheinungen untersucht werden.